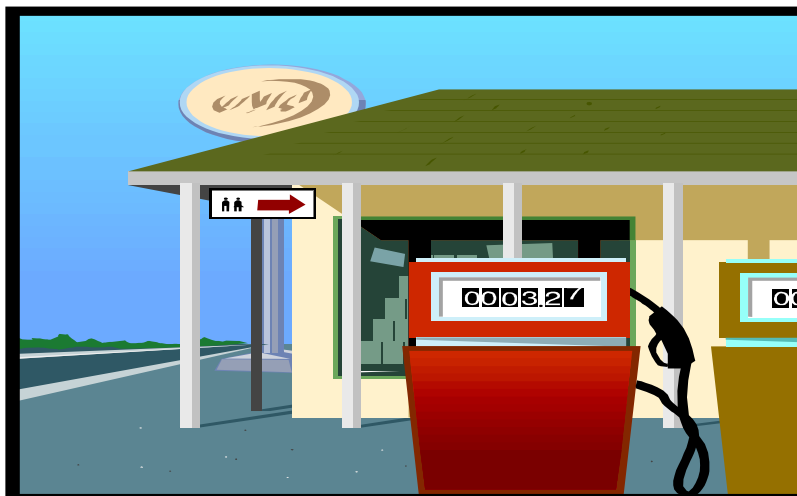


# DRAFT

## Developing Petroleum Hydrocarbon Cleanup Levels



Washington Department of Ecology  
Toxics Cleanup Program  
August 15, 2001

Publication No. 01-09-074



# Developing Petroleum Hydrocarbon Cleanup Levels

August 15, 2001

## What is this?

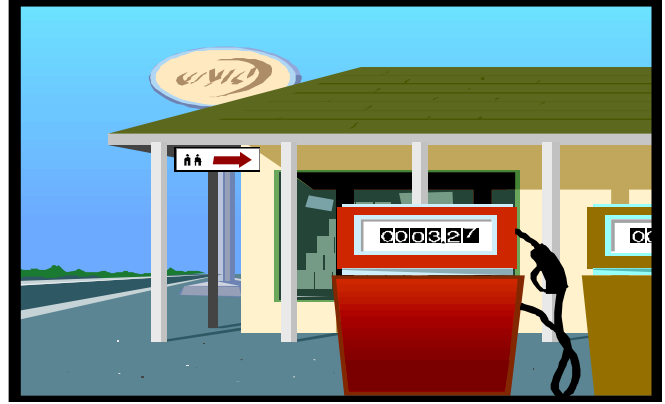
### *DRAFT TPH Guidance*

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Enclosed is Ecology's first DRAFT on how to develop Total Petroleum Hydrocarbon (TPH) cleanup levels. This document is a work in progress – it only contains information on how to derive cleanup levels for the soil to groundwater exposure pathway. Ecology will be providing additional and detailed information on how to characterize the site, how to calculate cleanup levels and how to select remedies.

The enclosed draft was written in support of Ecology's instruction manual on how to use computer spreadsheets to derive TPH cleanup levels (*"Workbook Tools for Calculating Soil and Ground Water Cleanup Levels under the Model Toxics Control Act Cleanup Regulation"*, August 15, 2001). In summary, Ecology will be publishing two documents: (1) instructions on "how to" use the computer spreadsheet to derive TPH cleanup levels and (2) TPH guidance.

Ecology has envisioned that the guidance on "how to" calculate TPH cleanup levels is one piece of the commercial gas station model remedy.



Ecology views this as an on-going process and it will take time to develop all aspects of the model remedy.

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# 1 Introduction

## 1.1 Overview

This document provides users guidance on how to define the *input* parameters that are necessary to evaluate the *soil to ground water pathway* for the development of soil cleanup levels, including the following:

- Defining the nature and extent of petroleum contamination, including the composition of the petroleum mixture; and
- Defining the hydrogeological characteristics of the site.

These input parameters are used in the 3-phase and 4-phase equilibrium partitioning models to calculate soil concentrations that are protective of ground water under Method B and Method C.

This document *DOES NOT* currently provide instructions on how to calculate Method B or Method C cleanup levels. You will need to use the “MTCATPH.xls” computer spreadsheet to calculate Method B or Method C soil cleanup levels for the soil to ground water exposure pathway.

Also, this document does not provide instructions on how to evaluate or calculate cleanup levels for the:

- Direct contact pathway;
- Inhalation (vapor pathway); or
- Conduct a terrestrial ecological evaluation.

Ecology expects to expand the scope of this guidance document in the future.

## 1.2 Using Computer Spreadsheets (Workbook Tools) to Calculate Protective Soil Concentrations

Ecology has designed two computer workbooks, "MTCATPH.xls" and "MTCASGL.xls", which enable users to calculate soil and ground water cleanup levels for petroleum mixtures and single chemicals respectively. To facilitate the use of these workbooks, Ecology has published the following manual:

*Workbook Tools for Calculating Soil and Ground Water Cleanup Levels under the Model Toxics Control Act Cleanup Regulation – User's Guide*, Pub. No. 01-09-073, Aug. 2001.

The workbooks allow the user to input site-specific values for the input parameters described in this document to evaluate the soil to ground water exposure pathway and to calculate a protective soil concentration.

### WARNING

The soil cleanup levels calculated using the workbook tools DO NOT account for the following:

- Concentrations established under applicable state and federal laws;
- Concentrations based on protection of air quality (vapor pathway);
- Concentrations based on protection of terrestrial ecological receptors;
- Residual saturation limit for protection of ground water; and

- Total site risk (where the release includes chemicals other than those related to a petroleum mixture).



## 2 Site Characterization

### 2.1 Overview

This chapter provides information on petroleum hydrocarbon site characterization. It contains instructions on how to derive three key components for the soil to ground water exposure pathway:

- Petroleum hydrocarbon concentrations / composition,
- Hydrogeologic parameters (e.g. soil organic carbon, dilution factor, etc.), and
- Residual saturation.

The objective of site characterization is to:

- Derive a conceptual site model, which is the “cornerstone” of the commercial gas station cleanup level process.
- Delineate the nature and extent of all soil, air and water petroleum hydrocarbon contamination, and

### 2.2 Regulatory Requirements

Commercial gas station owner / operators who have had a release from an underground storage tank (UST) are required to submit a site characterization report to Ecology within ninety days of confirmation of a release and this report must include the information specified in WAC 173-340-450 (5) (b).

### 2.3 Site Characterization for the Soil to Ground Water Exposure Pathway

For the soil to ground water exposure pathway, Ecology recommends that you focus your site characterization efforts on three key variables:

- Petroleum hydrocarbon concentration / composition,
- Hydrogeologic parameters (e.g. soil organic carbon, dilution factor, etc.), and
- Residual saturation.

The chapter contains detailed information on how to derive values for each one of these three variables.

### 2.4 Deriving Petroleum Hydrocarbon Concentration / Composition

#### 2.4.1 Analytical Requirements

Commercial gas station owner / operators will need to analyze both the soil and ground water for the hazardous substances specified in Table 830-1. This table is divided into five petroleum hydrocarbon categories: gasoline range organics (GRO), diesel range organics (DRO), heavy oils, mineral oils and waste / unknown oils. The soil and ground water testing requirements vary depending upon the petroleum category.

If you don't know the type (e.g. gasoline, diesel, etc.) of petroleum hydrocarbons present, you will need to first qualitatively identify using the

NWTPH-HCID<sup>1</sup> analytical method. Further quantitation of the type of fuel present may be accomplished using NWTPH-G<sup>2</sup> or NWTPH-Dx<sup>3</sup> analytical methods. If a mixture of petroleum hydrocarbons is present (e.g. gasoline and diesel), then you will need to test for the components specified for both types of fuels.

#### 2.4.2 Total Petroleum Hydrocarbons (TPH)

To derive site-specific residential or industrial total petroleum hydrocarbon (TPH) soil cleanup levels for the direct contact and soil to ground water exposure pathways, you will need to analyze the soil for the petroleum hydrocarbon EC “fractions”. Use the

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<sup>1</sup> **NWTPH-HCID:** this method is a qualitative and semi-quantitative procedure. It is used for ground water or surface water, and soil/sediment from sites where the petroleum products are unknown and/or when multiple types of petroleum products are suspected to be present. This method is used to identify petroleum products containing components from C7 to C30 range, as well as heavy oils, with specific product confirmation by pattern matching (“fingerprinting”) employing capillary gas chromatography with flame ionization detection (GC/FID). EPA method 3510 has been adapted as the extraction procedure for the water portion of this method.

<sup>2</sup> **NWTPH-Gx** is the qualitative and quantitative method (extended) for volatile (“gasoline”) petroleum products in soil and water. Petroleum products applicable for this method include aviation and automotive gasolines, mineral spirits, stoddard solvent and naphtha.

<sup>3</sup> **NWTPH-Dx** is the qualitative and quantitative method (extended) for semi-volatile (“diesel”) petroleum products in soil and water. Petroleum products applicable for this include jet fuels, kerosene, diesel oils, hydraulic fluids, mineral oils, lubricating oils and fuel oils.

Volatile Petroleum Hydrocarbons (VPH) analytical method for gasoline range organics (GRO) and the Extractable Range Hydrocarbons (EPH) for diesel range organics (DRO) and heavy fuel oils.

#### 2.4.3 Volatile Petroleum Hydrocarbons (VPH)

The VPH method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil. Carbon ranges are given in equivalent carbon (EC) numbers which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes, and its retention time in a boiling point gas chromatographic (GC) column.

Volatile aliphatic hydrocarbons are collectively quantitated within four ranges: C5 through C6, >C6 through C8, >C8 through C10 and > C10 through C12. Volatile aromatic hydrocarbons are collectively quantitated within the C8 through C10, >C10 through C12 and >C12 through C13 ranges. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

This method is also designed to measure the individual concentrations of benzene, toluene, ethylbenzene, xylenes, and methyl tert butylether (MTBE) in water and soil.

#### 2.4.4 Extractable Petroleum Hydrocarbons (EPH)

The EPH method is designed to measure the collective concentrations of extractable aliphatic and aromatic

petroleum hydrocarbons in water and soil. Carbon ranges are given in equivalent carbon numbers (EC) which are related to the boiling point of a chemical normalized to the boiling point of the n-alkanes and its retention time in a boiling point gas chromatographic column.

Extractable aliphatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. Extractable aromatic hydrocarbons are collectively quantitated within five ranges: C8 through C10, >C10 through C12, >C12 through C16, >C16 through C21 and >C21 through C34. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 150 °C and 500 °C.

#### 2.4.5 “Double Counting”

Because the VPH and EPH analytical methods overlap carbon ranges, you will need to make sure that you don’t “double count” fractions. If the VPH method is used for gasoline, you will need to subtract E and X from the Aromatic 8-10 EC range and you will also need to subtract naphthalene from the Aromatic EC 12-16 range (Table 1).

**Table 1: Adjusting VPH Data (Example).**

Hazardous Substance	*Reported mg/kg	Adjustment	Adj. Value mg/kg
B	19,800	None	19,800
T	52,400	None	52,400
E	11,600	None	11,600
X	60,800	None	60,800
Aromatic C8-C10	110,000	-(E + X)	37,600
Aromatic	45,100	- Naphthalene	33,900

C12-C13			
Naphthalene	11,200	None	11,200

\* Reported values are for neat (pure) gasoline (Ecology fuel / water mixing experiment data, unpublished). BTEX and Naphthalene analyzed by GC / PID.

#### 2.4.6 Individual Components

You will also need to analyze the soil for individual components (e.g., benzene). For gasoline range organics, BTEX components are included in the VPH method; however, for diesel range organics (DRO), naphthalene and carcinogenic polycyclic aromatic hydrocarbons (cPAHs) are not included. You will need to ask the laboratory about analysis for these components.

#### 2.4.7 Deriving a Representative Hydrocarbon Composition

For commercial gas station sites, one item of particular importance is the petroleum hydrocarbon composition ratios. The amount or percentage of each EC fraction and individual component (BTEX) will vary and you will need to collect enough samples to establish a “representative” composition.

To obtain a representative composition, you will need to collect soil samples from the source area. In most cases, you will at a minimum need to collect 3 to 5 soil samples to obtain a representative composition.

### **2.5 Hydrogeologic Parameters**

#### 2.5.1 Mass Fraction of Natural Soil Organic Carbon (foc)

For the soil to ground water exposure pathway, the mass fraction of natural soil organic carbon (foc) samples is a

highly sensitive model input parameter. In most cases, the amount of soil organic carbon will decrease with depth. Consequently, mass fraction of natural soil organic carbon (foc) samples need to be obtained from soil beneath the root zone (depth of at least 1 meter) and they will also need to be obtained from areas that are not contaminated with petroleum hydrocarbons.

Ecology uses a default value of 0.1% soil foc (0.001-gram soil organic per gram soil). The 0.1% foc value is based on information from the scientific literature, cleanup sites and feedback from Ecology's Science Advisory Board (SAB).

### 2.5.2 Soil Organic Carbon Analysis

The 1986 Puget Sound Estuary Program Total Organic Carbon (TOC) method is an acceptable method for measuring organic carbon. In this method, the sample is first prepped with HCL to remove inorganic carbon. The sample is then combusted in an induction furnace @ 950° C, which releases all inorganic and carbon in the form of CO<sub>2</sub>.

Measuring the amount of CO then derives the carbon content of the sample. You will need a minimum sample size of 25 grams for this method.

If you have a soil sample with high concentrations of carbonate or bicarbonate, then you may need to check with the lab, as inorganic carbon will bias the measurement (make sure the laboratory dissolves all of the inorganic carbon prior to analysis). The lab will also need to be careful about the type and amount of acid used as this may also bias the test.

### 2.5.3 Porosity, Density, Volumetric Air and Water Content

These five input parameters will in most cases not have a significant impact on your calculations for the soil to ground water exposure pathway; however, they may be important for the vapor exposure pathway. You may use the default values provided in Table 2 or site-specific measurements. Any soils or geotechnical laboratory should be able to analyze soil samples for these parameters at nominal cost.

**Table 2: Soil Porosity, Volumetric Air / Water Content and Bulk Density.**

Parameter		Value	Units
Porosity	n	0.43	mL <sub>VOID</sub> /mL <sub>SOIL</sub>
Volumetric Water Content	$\theta_w$	0.3	mL <sub>WATER</sub> /mL <sub>SOIL</sub>
Volumetric Air Content	$\theta_a$	0.13	mL <sub>AIR</sub> /mL <sub>SOIL</sub>
Bulk Density	$\rho_b$	1.5	kg / L

### 2.5.4 Dilution Factor

Concentration "dilution" occurs when petroleum hydrocarbons migrate vertically through the soil and mix with ground water. This concentration reduction is accounted for by use of a dimensionless term known as the "dilution factor".

Ecology uses a simple "box" model to simulate this dilution (Figure 1). This model is based on two components: the volume of water infiltrating and the volume of water flowing through the aquifer.

To calculate a site-specific dilution factor, you will need to derive two variables, the ground water flow volume

( $Q_a$ ) and the infiltration volume ( $Q_p$ ) (Equation 1). Information on how to derive both of these parameters is provided in this section.

$$\text{Equation 1: } DF = \frac{Q_p + Q_a}{Q_p}$$

DF	Dilution factor (dimensionless)
$Q_p$	Volume of water infiltrating ( $m^3/yr$ )
$Q_a$	Ground water flow volume ( $m^3/yr$ )

Equation 1 is based on a simple dilution model (Figure 1).

### 2.5.5 Ground Water Flow Volume

To calculate the ground water flow volume ( $Q_a$ ), you will need to derive values for two input parameters: hydraulic conductivity and gradient.

To derive site-specific hydraulic conductivity (K) values, you will need to:

- Conduct an aquifer pump test,
- Conduct a slug test, or
- Use the Hazen method<sup>4</sup> to derive K.

A site-specific hydraulic conductivity value may then be used in (Equation 2) to calculate a ground water flow volume.

$$\text{Equation 2: } Q_a = KAI$$

<sup>4</sup> The Hazen method is based on the  $D_{10}$  grain size. You will need to have your soil sample sieved to generate a grain size distribution curve.

$Q_a$	Ground water flow volume ( $m^3/yr$ )
K	Hydraulic conductivity (cm/s)
A	Aquifer mixing zone ( $m^2$ )
I	Gradient (m/m)

Unless it can be empirically demonstrated otherwise, the depth of the Equation 2 aquifer-mixing zone must not exceed 5 meters and the width must be equal to 1 meter.

### 2.5.6 Infiltration

Table 7 has infiltration values for thirty-six (36) Washington cities. You may use the Table 7 values or make a site-specific measurement of infiltration using soil that is not covered (e.g. concrete or asphalt). A percentage of the mean annual precipitation rate was used to generate the Table 7 infiltration values. For Western Washington, this percentage was 70%; for Eastern Washington, this percentage was 30%. Use Equation 3 to calculate the volume of infiltration.

$$\text{Equation 3: } Q_p = LWI_{nf}$$

$Q_p$	Volume of water infiltrating ( $m^3/yr$ )
L	Estimated length of contaminant source area parallel to ground water flow (m)
W	Width of contaminant source area (1 m).
$I_{nf}$	Infiltration (in/yr)

### 2.5.7 Where Should Soil Samples be Collected?

- For the soil to ground water exposure pathway, you should collect samples from ground surface down to the ground water table.

## 2.6 Residual Saturation

For the soil to ground water exposure pathway, you will need to check and make sure that the TPH soil cleanup level does not exceed residual saturation (WAC 173-340-747 (10)).

Consequently, you may need or want to measure residual saturation during the site-characterization process. If you don't measure residual saturation, then you will need to compare the soil to ground water exposure pathway cleanup levels against the default values provided in Table 3.

**Table 3: Residual Saturation Screening Levels for TPH.**

Fuel	Screening Level (mg/kg)
Weathered Gasoline	1,000
Middle Distillates (e.g., Diesel No. 2 Fuel Oil)	2,000
Heavy Fuel Oils (e.g., No. 6 Fuel Oil)	2,000
Mineral Oil	4,000
Unknown Composition or Type	1,000

**Note:** The residual saturation screening levels for petroleum hydrocarbons specified in this table are based on coarse sand and gravelly soils; however, they may be used for any soil type. Screening levels are based on the presumption that there are no preferential pathways for NAPL to flow downward to ground water. If such pathways exist, more stringent residual saturation screening levels may need to be established.

### 2.6.1 Definition

The term “residual saturation” is used to describe the phenomenon that occurs when petroleum hydrocarbons are “trapped” within the soil pores. Specifically, when petroleum hydrocarbons are released to the soil, a

certain percentage will be “bound” into the soil matrix by capillary forces and molecular attraction. “Residual saturation” is the percentage of petroleum hydrocarbons bound within the soil.

Saturation of the soil-system with petroleum hydrocarbons will at some point result in the downward force of gravity exceeding the soil's ability to retain petroleum hydrocarbons by capillary forces and molecular attraction. Petroleum hydrocarbons will vertically migrate as a separate non-aqueous phase liquid (NAPL) phase when this occurs.

### 2.6.2 Factors that Control Residual Saturation

Residual saturation is primarily a function of three factors: soil texture or particle size, soil moisture content and the viscosity of the petroleum hydrocarbon itself.

For example, very fine soils (e.g., fine sand) with very little moisture content (0.1 ml water per ml soil) will have a much higher petroleum hydrocarbon residual saturation level. Conversely, coarse soils (e.g., gravel) with a moisture content of 0.3 or higher will likely have a residual saturation level that is much lower. Lastly, highly viscous oil (e.g. No. 6 or Bunker C) tends to have much higher soil residual saturation levels.

### 2.6.3 Units

Residual saturation ( $s_r$ ) may be expressed in dimensionless form as the volume of fuel per pore space volume:

**Equation 4:** 
$$s_r = \frac{R}{n * 1000}$$

$S_r$	Residual saturation (dimensionless)
$R$	Volumetric retention capacity (Liters of fuel / $m^3$ soil)
$n$	Soil porosity (dimensionless)

#### 2.6.4 Converting Residual Saturation to an Equivalent Soil Concentration

Use Equation 5 to convert residual saturation to an equivalent soil concentration:

$$\text{Equation 5: } S = \left[ \frac{R * \rho_{\text{FUEL}} * 1000}{\rho_b} \right]$$

$S$	Equivalent Soil Concentration (mg/kg)
$R$	Volumetric retention capacity (liters of residual NAPL per cubic meter of soil)
$\rho_{\text{FUEL}}$	Fuel Density (kg / L)
$\rho_b$	Soil Bulk Density (1.5 kg / L)

For fuel density ( $\rho_{\text{FUEL}}$ ) you may use:

- The equilibrated weighted average molecular weight of the fuel (g/mol; see the lower right corner of workbook “A2” of the “MTCATPH.xls” spreadsheet), or
- The fuel densities provided in Table 4.

**Table 4: Fuel Density.**

Fuel	Density (kg / L)
Gasoline	0.734
Diesel	0.83 – 0.854
Heavy Fuel Oil (No. 6)	0.909 – 0.925

Source: Shiu et al. (1990)

#### 2.6.5 Measuring Residual Saturation

Ecology does not have any standard protocols for measuring residual saturation. If you do decide to measure residual saturation, you will also need to check or account for chemical partitioning. For example, residual saturation is not likely to be a limiting factor for fuels like gasoline because of benzene partitioning to the water-phase. In most cases, Ecology expects that residual saturation will be most useful for sites with diesel or heavy fuel oils because chemical partitioning<sup>5</sup> is less of an issue for these fuels.

<sup>5</sup> Diesel fuel and heavy fuel oil (No. 6) typically have trace levels (< 0.1%) of benzene; however, they do contain naphthalene and substituted naphthalenes (i.e. 2-methyl) and these components will partition from the fuel into water. You will need to check and make sure that naphthalene partitioning to the water phase is not issue when deriving residual saturation for diesel and heavier fuels.

**Table 5: Petroleum Hydrocarbon Toxicity and Physical Chemical Values.**

TPH Component / Fraction	Equivalent Carbon (EC) Number <sup>1</sup>	Oral Reference Dose (mg-kg/day)	Water Solubility <sup>2</sup> (mg/L)	Molecular Weight <sup>3</sup> (g/mol)	Henry's Constant <sup>4</sup> (cc/cc)	Gram Formula Weight <sup>5</sup> (mg/mol)	Density <sup>6</sup> (mg/l)	Soil Organic Carbon-Water Partitioning Coefficient Koc <sup>7</sup> (L/kg)
<b>Aliphatics</b>								
EC > 5 – 6	5.5	5.7	36.0	81.0	33.0	81,000	670,000	800
EC > 6 – 8	7.0	5.7	5.4	100.0	50.0	100,000	700,000	3,800
EC > 8 – 10	9.0	0.03	0.43	130.0	80.0	130,000	730,000	30,200
EC > 10 – 12	11.0	0.03	0.034	160.0	120.0	160,000	750,000	234,000
EC > 12 – 16	14.0	0.03	7.6E-04	200.0	520.0	200,000	770,000	5.37E+06
EC > 16 – 21	19.0	2	1.3 E-06	270.0	4,900	270,000	780,000	9.55E+09
EC > 21 – 34	28.0	2	1.5E-11	400.0	100,000	400,000	790,000	1.07E+10
<b>Aromatics</b>								
EC > 8 – 10	9.0	0.05	65.0	120.0	0.48	120,000	870,000	1,580
EC > 10 – 12	11.0	0.05	25.0	130.0	0.14	130,000	900,000	2,510
EC > 12 – 16	14.0	0.05	5.8	150.0	0.053	150,000	1,000,000	5,010
EC > 16 – 21	19.0	0.03	0.51	190.0	0.013	190,000	1,160,000	15,800
EC > 21 – 34	28.0	0.03	6.6E-03	240.0	6.7E-04	240,000	1,300,000	126,000
<b>Individual</b>								
Benzene	6.5	0.003	1,750	78.0	0.228	78,000	876,500	62.0
Toluene	7.6	0.2	526.0	92.0	0.272	92,000	866,900	140.0
Ethylbenzene	8.5	0.1	169.0	106.0	0.323	106,000	867,000	204.0
Total Xylenes <sup>8</sup>	8.67	2	171.0	106.0	0.279	106,000	875,170	233.0
n-Hexane <sup>9</sup>	6.0	0.06	9.5	86.0	74.0	86,000	659,370	3,410
MTBE <sup>10</sup>			50,000	88.0	0.018	88,000	744,000	10.9
Naphthalenes	11.69	0.02	31.0	128.0	0.0198	128,000	1,145,000	1,191

**1 Equivalent Carbon Number.** Gustafson, J.B. et al., *Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Total Petroleum Hydrocarbon Criteria Working Group Series*, Volume 3 (1997) [hereinafter *Criteria Working Group*].

**2 Water Solubility.** For aliphatics and aromatics EC groups, *Criteria Working Group*. For TPH components except n-hexane and MTBE, *1996 EPA Soil Screening Guidance: Technical Background Document*.

**3 Molecular Weight.** *Criteria Working Group*.

**4 Henry's Constant.** For aliphatics and aromatics EC groups, *Criteria Working Group*. For TPH components except n-hexane and MTBE, *1996 EPA Soil Screening Guidance: Technical Background Document*.

**5 Gram Formula Weight (GFW).** Based on 1000 x Molecular Weight.

**6 Density.** For aliphatics and aromatics EC groups, based on correlation between equivalent carbon number and data on densities of individual hazardous substances provided in *Criteria Working Group*. For TPH components except n-hexane and MTBE, *1996 EPA Soil Screening Guidance: Technical Background Document*.

**7 Soil Organic Carbon-Water Partitioning Coefficient.** For aliphatics and aromatics EC groups, *Criteria Working Group*. For TPH components except n-hexane and MTBE, *1996 EPA Soil Screening Guidance: Technical Background Document*.

**8 Total Xylenes.** Values for total xylenes are a weighted average of m, o and p xylene based on gasoline composition data from the *Criteria Working Group* (m= 51% of total xylene; o = 28% of total xylene; and p = 21% of total xylene).

**9 n-Hexane.** For values other than density, *Criteria Working Group*. For the density value, *Hawley's Condensed Chemical Dictionary*, 11<sup>th</sup> ed., revised by N. Irving Sax and Richard J. Lewis (1987).

**10 MTBE.** *USGS Final Report on Fuel Oxygenates* (March 1996).



**Table 830-1: Required Testing for Petroleum Releases.**

	<b>Gasoline Range Organics (GRO) (1)</b>	<b>Diesel Range Organics (DRO) (2)</b>	<b>Heavy Oils (DRO) (3)</b>	<b>Mineral Oils (4)</b>	<b>Waste Oils and Unknown Oil (5)</b>
<b>Volatile Petroleum Compounds</b>					
Benzene	X (6)	X (7)			X (8)
Toluene	X (6)	X (7)			X (8)
Ethyl benzene	X (6)	X (7)			X (8)
Xylenes	X (6)	X (7)			X (8)
n-Hexane	X (9)				
<b>Fuel Additives and Blending Compounds</b>					
Dibromoethane, 1-2 (EDB); and Dichloroethane, 1-2 (EDC)	X (10)				X (8)
Methyl tertiary-butyl ether (MTBE)	X (11)				X (8)
Total Lead and Other Additives	X (12)				X (8)
<b>Other Petroleum Components</b>					
Carcinogenic PAHs		X (13)	X (13)		X (8)
Naphthalenes	X (14)	X (14)	X (14)		X (14)
<b>Other Compounds</b>					
Polychlorinated Biphenyls (PCBs)			X (15)	X (15)	X (8)
Halogenated Volatile Organic Compounds (VOCs)					X (8)
Other	X (16)	X (16)	X (16)	X (16)	X (16)
<b>Total Petroleum Hydrocarbons Methods</b>					
TPH Analytical Method for Total TPH (Method A Cleanup Levels) (17)	NWTPH-Gx	NWTPH-Dx	NWTPH-Dx	NWTPH-Dx	NWTPH-Gx & NWTPH-Dx
TPH Analytical Methods for TPH fractions (Methods B or C) (17)	VPH	EPH	EPH	EPH	VPH and EPH

[Editor's Note: See next page for the footnotes associated with Table 830-1.]

**Use of Table 830-1:** An "X" in the box means that the testing requirement applies to ground water and soil if a release is known or suspected to have occurred to that medium, unless otherwise specified in the footnotes. A box with no "X" indicates (except in the last two rows) that, for the type of petroleum product release indicated in the top row, analyses for the hazardous substance(s) named in the far-left column corresponding to the empty box are not typically required as part of the testing for petroleum releases. However, such analyses may be required based on other site-specific information. Note that testing for Total Petroleum Hydrocarbons (TPH) is required for every type of petroleum release, as indicated in the bottom two rows of the table. The testing method for TPH depends on the type of petroleum product released and whether Method A or Method B or C is being used to determine TPH cleanup levels. See WAC 173-340-830 for analytical procedures. **The footnotes to this table are important for understanding the specific analytical requirements for petroleum releases.**

**Footnotes:**

- (1) The following petroleum products are common examples of GRO: automotive and aviation gasolines, mineral spirits, stoddard solvents, and naphtha. To be in this range, 90 percent of the petroleum components need to be quantifiable using the NWTPH-Gx; if NWTPH-HCID results are used for this determination, then 90 percent of the "area under the TPH curve" must be quantifiable using NWTPH-Gx. Products such as jet fuel, diesel No. 1, kerosene, and heating oil may require analysis as both GRO and DRO depending on the range of petroleum components present (range can be measured by NWTPH-HCID). (See footnote 17 on analytical methods.)
- (2) The following petroleum products are common examples of DRO: Diesel No. 2, fuel oil No. 2, light oil (including some bunker oils). To be in this range, 90 percent of the petroleum components need to be quantifiable using the NWTPH-Dx quantified against a diesel standard. Products such as jet fuel, diesel No. 1, kerosene, and heating oil may require analysis as both GRO and DRO depending on the range of petroleum components present as measured in NWTPH-HCID.
- (3) The following petroleum products are common examples of the heavy oil group: Motor oils, lube oils, hydraulic fluids, etc. Heavier oils may require the addition of an appropriate oil range standard for quantification.
- (4) Mineral oil means non-PCB mineral oil, typically used as an insulator and coolant in electrical devices such as transformers and capacitors.
- (5) The waste oil category applies to waste oil, oily wastes, and unknown petroleum products and mixtures of petroleum and nonpetroleum substances. Analysis of other chemical components (such as solvents) than those listed may be required based on site-specific information. Mixtures of identifiable petroleum products (such as gasoline and diesel, or diesel and motor oil) may be analyzed based on the presence of the individual products, and need not be treated as waste and unknown oils.
- (6) When using Method A, testing soil for benzene is required. Furthermore, testing ground water for BTEX is necessary when a petroleum release to ground water is known or suspected. If the ground water is tested and toluene, ethyl benzene or xylene is in the ground water above its respective Method A cleanup level, the soil must also be tested for that chemical. When using Method B or C, testing the soil for BTEX is required and testing for BTEX in ground water is required when a release to ground water is known or suspected.
- (7)(a) For DRO releases from other than home heating oil systems, follow the instructions for GRO releases in Footnote (6).
- (b) For DRO releases from typical home heating oil systems (systems of 1,100 gallons or less storing heating oil for residential consumptive use on the premises where stored), testing for BTEX is not usually required for either ground water or soil. Testing of the ground water is also not usually required for these systems; however, if the ground water is tested and benzene is found in the ground water, the soil must be tested for benzene.
- (8) Testing is required in a sufficient number of samples to determine whether this chemical is present at concentrations of concern. If the chemical is found to be at levels below the applicable cleanup level, then no further analysis is required.
- (9) Testing for n-hexane is required when VPH analysis is performed for Method B or C. In this case, the concentration of n-hexane should be deleted from its respective fraction to avoid double-counting its concentration. n-Hexane's contribution to overall toxicity is then evaluated using its own reference dose.
- (10) Volatile fuel additives (such as dibromoethane, 1-2 (EDB) (CAS# 106-93-4) and dichloroethane, 1-2 (EDC) (CAS# 107-06-2)) must be part of a volatile organics analysis (VOA) of GRO contaminated ground water. If any is found in ground water, then the contaminated soil must also be tested for these chemicals.
- (11) Methyl tertiary-butyl ether (MTBE) (CAS# 1634-04-4) must be analyzed in GRO contaminated ground water. If any is found in ground water, then the contaminated soil must also be tested for MTBE.
- (12)(a) For automotive gasoline where the release occurred prior to 1996 (when "leaded gasoline" was used), testing for lead is required unless it can be demonstrated that lead was not part of the release. If this demonstration cannot be made, testing is required in a sufficient number of samples to determine whether lead is present at concentrations of concern. Other additives and blending compounds of potential environmental significance may need to be considered for testing, including: tertiary-butyl alcohol (TBA); tertiary-amyl methyl ether (TAME); ethyl tertiary-butyl ether (ETBE); ethanol; and methanol. Contact the department for additional testing recommendations regarding these and other additives and blending compounds.
- (b) For aviation gasoline, racing fuels and similar products, testing is required for likely fuel additives (especially lead) and likely blending compounds, no matter when the release occurred.
- (13) Testing for carcinogenic PAHs is required for DRO and heavy oils, except for the following products for which adequate information exists to indicate their absence: Diesel No. 1 and 2, home heating oil, kerosene, jet fuels, and electrical insulating mineral oils. The carcinogenic PAHs include benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, benzo(k)fluoranthene, benzo(a)anthracene, and benzo(b)fluoranthene.
- (14)(a) Except as noted in (b) and (c), testing for the non-carcinogenic PAHs, including the "naphthalenes" (naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene) is not required when using Method A cleanup levels, because they are included in the TPH cleanup level.
- (b) Testing of soil for naphthalenes is required under Methods B and C when the inhalation exposure pathway is evaluated.
- (c) If naphthalenes are found in ground water, then the soil must also be tested for naphthalenes.
- (15) Testing for PCBs is required unless it can be demonstrated that: (1) the release originated from an electrical device manufactured for use in the United States after July 1, 1979; (2) oil containing PCBs was never used in the equipment suspected as the source of the release (examples of equipment where PCBs are likely to be found include transformers, electric motors, hydraulic systems, heat transfer systems, electromagnets, compressors, capacitors, switches and miscellaneous other electrical devices); or, (3) the oil released was recently tested and did not contain PCBs.
- (16) Testing for other possible chemical contaminants may be required based on site-specific information.
- (17) The analytical methods NWTPH-Gx, NWTPH-Dx, NWTPH-HCID, VPH, and EPH are methods published by the Department of Ecology and available on the department's Internet web site: <http://www.ecy.wa.gov/programs/tcp/cleanup.html>.

**Table 6: Default Fuel Compositions.**

	Fresh Gasoline	Weathered Gasoline	Fresh Diesel	Weathered Diesel	Heavy Fuel Oil
<u>Aliphatic</u>					
AL >5-6	28.48%	2.64%	0.06%	0.003%	
AL >6-8	17.18%	14.13%	0.31%	0.12%	
AL >8-10	4.59%	9.94%	1.02%	0.91%	0.57%
AL >10-12	5.52%	13.81%	4.18%	4.19%	1.25%
AL >12-16			29.98%	30.46%	10.64%
AL >16-35			42.55%	43.28%	60.63%
<u>Aromatic</u>					
AR >8-10	5.52%	10.25%	0.75%	0.57%	
AR >10-12	9.22%	20.24%	3.53%	3.15%	0.57%
AR >12-16	6.62%	16.11%	9.67%	9.47%	0.83%
AR >16-21			7.60%	7.70%	4.48%
AR >21-35			0.07%	0.07%	21.03%
B	2.91%	0.13%	0.01%	0.0002%	
T	7.69%	2.00%	0.03%	0.004%	
E	1.70%	1.14%	0.02%	0.01%	
X	8.93%	6.43%	0.11%	0.04%	
Naphthalene	1.64%	3.20%	0.03%	0.02%	
	100.00%	100.00%	99.92%	100.00%	100.00%

Note: the composition ratios published in this table are for information purposes only. You may use them to check site conditions; however, site-specific (Method B or C) soil cleanup levels must be based on site-specific VPH or EPH measurements (see Section 2.4, p. 3).

**Table 7: State of Washington Mean Annual Precipitation and Infiltration.**

<b>Western WA City</b>	<b>Mean Annual Precipitation in/yr</b>	<b>* Infiltration in/yr</b>	<b>Eastern WA City</b>	<b>Mean Annual Precipitation in/yr</b>	<b>**Infiltration in/yr</b>
Aberdeen	82.96	58.07	Colfax	20.3	6.09
Battle Ground	47.22	33.05	Colville	16.54	4.96
Bellingham	33.96	23.77	Coupeillie	18.64	5.59
Centralia	44.77	31.34	Dayton	20.5	6.15
Clearwater	125.26	87.68	Ellensburg	8.53	2.56
Everett	32.46	22.72	Ephrate	7.91	2.37
Forks	115.14	80.60	Goldendale	16.22	4.87
Longview	40.59	28.41	Kennewick	7.06	2.12
Mt. Baker Lodge	109.49	76.64	Newport	23.15	6.95
Olga	28.98	20.29	Omak	11.27	3.38
Olympia	45.74	32.02	Pomeroy	17.24	5.17
Port Angeles	27.36	19.15	Prosser	7.56	2.27
Rainier-Paradise	98.2	68.74	Ritzville	10.62	3.19
Seattle	31.92	22.34	Sequim	16.06	4.82
Sedro Wolley	45.5	31.85	Spokane	14.92	4.48
Snoqualmie Pass	94.74	66.32	Walla Walla	15.07	4.52
Tacoma	35.2	24.64	Wenatchee	8.75	2.63
Willapa Harbor	82.59	57.81	Yakima	7.21	2.16

\* West Side infiltration values are 70% of the mean annual precipitation. \*\* East Side infiltration values are 30% of the mean annual precipitation. See WAC 173-340-747 (5) (f) (B).

**Table 8: Method A Soil Lookup Table Values – Petroleum Hydrocarbons (Unrestricted and Industrial Land Use).**

Hazardous Substance	Cleanup Level (mg/kg)
B – Benzene	0.030
T – Toluene	7.0
E – Ethyl Benzene	6.0
X – Xylenes	9.0
MTBE	0.1
EDB	0.005
Naphthalene	5.0
Benzo(a)pyrene	0.1 = residential 2.0 = industrial
GRO <sup>(1)</sup>	30.0
GRO (No Benzene & TEX Sum is 1% of Total)	100.0
DRO <sup>(2)</sup>	2,000
Heavy Oils <sup>(3)</sup>	2,000
Mineral Oils <sup>(4)</sup>	4,000

(1) **GRO (Gasoline range organics)** means organic compounds measured using method NWTPH-Gx. Examples are aviation and automotive gasoline. The cleanup level is based on protection of ground water for noncarcinogenic effects during drinking water use using the procedures described in WAC 173-340-747(6). Two cleanup levels are provided. The lower value of 30 mg/kg can be used at any site. When using this lower value, the soil must also be tested for and meet the benzene soil cleanup level. The higher value of 100 mg/kg can only be used if the soil is tested and found to contain no benzene and the total of ethyl benzene, toluene and xylene are less than 1% of the gasoline mixture. No interpolation between these cleanup levels is allowed. In both cases, the soil cleanup level for any other carcinogenic components of the petroleum [such as EDB and EDC], if present at the site, must also be met. Also, in both cases, soil cleanup levels for any noncarcinogenic components [such as toluene, ethylbenzene, xylenes, naphthalene, and MTBE], also must be met if these substances are found to exceed ground water cleanup levels at the site. See Table 830-1 for the minimum testing requirements for gasoline releases.

(2) **DRO (Diesel range organics)** means organic compounds measured using method NWTPH-Dx. Examples are diesel, kerosene, and #1 and #2 heating oil. The

cleanup level is based on preventing the accumulation of free product on the ground water, as described in WAC 173-340-747(10). The soil cleanup level for any carcinogenic components of the petroleum [such as benzene and PAHs], if present at the site, must also be met. Soil cleanup levels for any noncarcinogenic components [such as toluene, ethylbenzene, xylenes and naphthalenes], also must be met if these substances are found to exceed the ground water cleanup levels at the site. See Table 830-1 for the minimum testing requirements for diesel releases.

(3) **Heavy oils** means organic compounds measured using NWTPH-Dx. Examples are #6 fuel oil, bunker C oil, hydraulic oil and waste oil. The cleanup level is based on preventing the accumulation of free product on the ground water, as described in WAC 173-340-747(10) and assuming a product composition similar to diesel fuel. The soil cleanup level for any carcinogenic components of the petroleum [such as benzene, PAHs and PCBs], if present at the site, must also be met. Soil cleanup levels for any noncarcinogenic components [such as toluene, ethylbenzene, xylenes and naphthalenes], also must be met if found to exceed the ground water cleanup levels at the site. See Table 830-1 for the minimum testing requirements for heavy oil releases.

(4) **Mineral oil** means non-PCB mineral oil, typically used as an insulator and coolant in electrical devices such as transformers and capacitors, measured using NWTPH-Dx. The cleanup level is based on preventing the accumulation of free product on the ground water, as described in WAC 173-340-747(10). Sites using this cleanup level must also analyze soil samples and meet the soil cleanup level for PCBs, unless it can be demonstrated that: (1) The release originated from an electrical device that was manufactured after July 1, 1979; or (2) oil containing PCBs was never used in the equipment suspected as the source of the release; or (3) it can be documented that the oil released was recently tested and did not contain PCBs. Method B or C must be used for releases of oils containing greater than 50 ppm PCBs. See Table 830-1 for the minimum testing requirements for mineral oil releases.



**Table 9: Method A Petroleum Hydrocarbon Ground Water Cleanup Levels<sup>(1)</sup>.**

Hazardous Substance	CAS Number	Cleanup Level
Benzene	71-43-2	5 ug/liter <sup>(2)</sup>
Benzo(a)pyrene	50-32-8	0.1 ug/liter <sup>(3)</sup>
1,2 Dichloroethane (EDC)	107-06-2	5 ug/liter <sup>(4)</sup>
Ethylbenzene	100-41-4	700 ug/liter <sup>(5)</sup>
Ethylene dibromide (EDB)	106-93-4	0.01 ug/liter <sup>(6)</sup>
MTBE	1634-04-4	20 ug/liter <sup>(7)</sup>
Naphthalenes	91-20-3	160 ug/liter <sup>(8)</sup>
PAHs (carcinogenic)		See benzo(a)pyrene <sup>(9)</sup>
Toluene	108-88-3	1,000 ug/liter <sup>(10)</sup>
Total Petroleum Hydrocarbons		
[Note: Must also test for and meet cleanup levels for other petroleum components--see footnotes!]		
Gasoline Range Organics		
Benzene present in ground water		800 ug/liter <sup>(11)(a)</sup>
No detectable benzene in ground water		1,000 ug/liter <sup>(11)(b)</sup>
Diesel Range Organics		
Heavy Oils		500 ug/liter <sup>(11)(c)</sup>
Mineral Oil		500 ug/liter <sup>(11)(d)</sup>
Xylenes	1330-20-7	500 ug/liter <sup>(11)(d)</sup>
		1,000 ug/liter <sup>(12)</sup>

**Footnotes:**

- (1) **Caution on misusing this table.** This table has been developed for specific purposes. It is intended to provide conservative cleanup levels for drinking water beneficial uses at sites undergoing routine cleanup actions or those sites with relatively few hazardous substances. This table may not be appropriate for defining cleanup levels at other sites. For these reasons, the values in this table should not automatically be used to define cleanup levels that must be met for financial, real estate, insurance coverage or placement, or similar transactions or purposes. Exceedances of the values in this table do not necessarily mean the ground water must be restored to those levels at all sites. The level of restoration depends on the remedy selected under WAC 173-340-350 through 173-340-390.
- (2) **Benzene.** Cleanup level based on applicable state and federal law (WAC 246-290-310 and 40 C.F.R. 141.61).
- (3) **Benzo(a)pyrene.** Cleanup level based on applicable state and federal law (WAC 246-290-310 and 40 C.F.R. 141.61), adjusted to a  $1 \times 10^{-5}$  risk. If other carcinogenic PAHs are suspected of being present at the site, test for them and use this value as the total concentration that all carcinogenic PAHs must meet using the toxicity equivalency methodology in WAC 173-340-708(8).
- (4) **1,2 Dichloroethane (ethylene dichloride or EDC).** Cleanup level based on applicable state and federal law (WAC 246-290-310 and 40 C.F.R. 141.61).
- (5) **Ethylbenzene.** Cleanup level based on applicable state and federal law (WAC 246-290-310 and 40 C.F.R. 141.61).
- (6) **Ethylene dibromide (1,2 dibromoethane or EDB).** Cleanup level based on concentration derived using Equation 720-2, adjusted for the practical quantitation limit.

- (7) **Lead.** Cleanup level based on applicable state and federal law (40 C.F.R. 141.80).
- (8) **Methyl tertiary-butyl ether (MTBE).** Cleanup level based on federal drinking water advisory level (EPA-822-F-97-009, December 1997).
- (9) **Naphthalenes.** Cleanup level based on concentration derived using Equation 720-1. This is a total value for naphthalene, 1-methyl naphthalene and 2-methyl naphthalene.
- (10) **Toluene.** Cleanup level based on applicable state and federal law (WAC 246-290-310 and 40 C.F.R. 141.61).
- (11) **Total Petroleum Hydrocarbons (TPH).** TPH cleanup values have been provided for the most common petroleum products encountered at contaminated sites. Where there is a mixture of products or the product composition is unknown, samples must be tested using both the NWTPH-Gx and NWTPH-Dx methods and the lowest applicable TPH cleanup level must be met.
- 11(a) **Gasoline range organics** means organic compounds measured using method NWTPH-Gx. Examples are aviation and automotive gasoline. The cleanup level is based on protection of ground water for noncarcinogenic effects during drinking water use. Two cleanup levels are provided. The higher value is based on the assumption that no benzene is present in the ground water sample. If any detectable amount of benzene is present in the ground water sample, then the lower TPH cleanup level must be used. No interpolation between these cleanup levels is allowed. The ground water cleanup level for any carcinogenic components of the petroleum [such as benzene, EDB and EDC] and any noncarcinogenic components [such as ethylbenzene, toluene, xylenes and MTBE], if present at the site, must also be met. See Table 830-1 for the minimum testing requirements for gasoline releases.
- 11(b) **Diesel range organics** means organic compounds measured using NWTPH-Dx. Examples are diesel, kerosene, and #1 and #2 heating oil. The cleanup level is based on protection from noncarcinogenic effects during drinking water use. The ground water cleanup level for any carcinogenic components of the petroleum [such as benzene and PAHs] and any noncarcinogenic components [such as ethylbenzene, toluene, xylenes and naphthalenes], if present at the site, must also be met. See Table 830-1 for the minimum testing requirements for diesel releases.
- 11(c) **Heavy oils** means organic compounds measured using NWTPH-Dx. Examples are #6 fuel oil, bunker C oil, hydraulic oil and waste oil. The cleanup level is based on protection from noncarcinogenic effects during drinking water use, assuming a product composition similar to diesel fuel. The ground water cleanup level for any carcinogenic components of the petroleum [such as benzene, PAHs and PCBs] and any noncarcinogenic components [such as ethylbenzene, toluene, xylenes and naphthalenes], if present at the site, must also be met. See Table 830-1 for the minimum testing requirements for heavy oil releases.
- 11(d) **Mineral oil** means non-PCB mineral oil, typically used as an insulator and coolant in electrical devices such as transformers and capacitors measured using NWTPH-Dx. The cleanup level is based on protection from noncarcinogenic effects during drinking water use. Sites using this cleanup level must analyze ground water samples for PCBs and meet the PCB cleanup level in this table unless it can be demonstrated that: (1) The release originated from an electrical device manufactured after July 1, 1979; or (2) oil containing PCBs was never used in the equipment suspected as the source of the release; or (3) it can be documented that the oil released was recently tested and did not contain PCBs. Method B (or Method C, if applicable) must be used for releases of oils containing greater than 50 ppm PCBs. See Table 830-1 for the minimum testing requirements for mineral oil releases.
- (12) **Xylenes.** Cleanup level based on xylene not exceeding the maximum allowed cleanup level in this table for total petroleum hydrocarbons and on prevention of adverse aesthetic characteristics. This is a total value for all xylenes.

Figure 1: Dilution Factor.

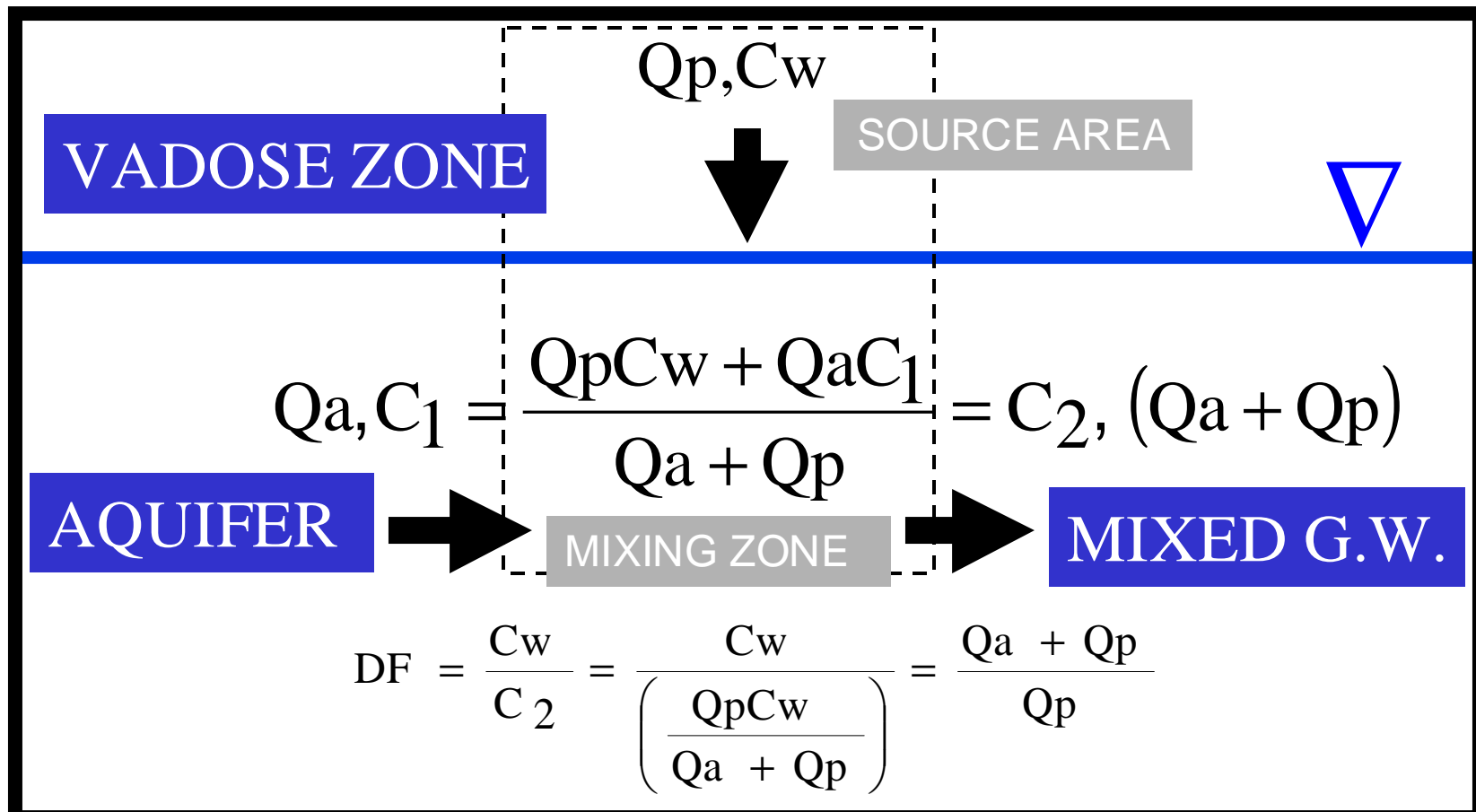
$Q_a$  = Ground Water Flow (m<sup>3</sup>/yr)

$Q_p$  = Infiltration (m<sup>3</sup>/yr)

$C_1$  = Background Concentration (mg/L)

$C_2$  = Concentration after Mixing (mg/L)

## DILUTION FACTOR





### 3 References

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